Crystal Phase-Controlled Synthesis of Cu_2FeSnS_4 Nanocrystals with Band Gap around 1.5 eV

Xiaoyan Zhang,[a,b] Ningzhong Bao,*[c] Karthik Ramasamy,[a] Yu-Hsiang A. Wang,[a] Yifeng Wang,[c] Baoping Lin[b] and Arunava Gupta*[a]

[a] Center for Materials for Information Technology, University of Alabama, Tuscaloosa, Alabama 35487, United States
[b] School of Chemistry and Chemical Engineering, Southeast University, Nanjing, P. R. China
[c] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing, P. R. China

Contents:

Experimental:

Chemicals:

Copper acetylacetonate ($Cu(acac)_2$; 99.99+%), Iron acetylacetonate ($Fe(acac)_3$; 99.99+%) from Aldrich; Tin Chloride ($SnCl_4 \cdot 5H_2O$); Oleylamine (OLA,~C18-content 80-90%), 1-octadecene (ODE, 90% tech), oleic acid (OA) from Acros Organics; 1-dodecanethiol (1-DDT, 98%) from Alfa Aesar, *tert*-Dodecyl Mercaptan (*t*-DDT) from TCI. All the chemicals and solvents were used as received without any further purification.

Characterization:

The morphology and size distribution of the nanocrystals were determined using transmission electron microscopy (TEM, FEI Tecnai F-20). For this purpose, the nanocrystals were dispersed in hexane and spray-dried on a TEM copper grid. X-ray powder diffraction (XRD, Bruker D8) was used to study the structure of the nanocrystals, and the optical property was measured using UV-Vis diffuse reflectance spectra (UV-Vis, Varian Cary 50). The samples for UV-Vis measurement were dispersed in hexane with ~0.02% OLA as surfactant. The composition of the nanocrystals was determined using Energy-dispersive X-ray spectroscopy (EDX).

Synthesis of Cu_2FeSnS_4 nanocrystals:

All the experiments were carried out in a fume hood under a N_2 atmosphere using standard Schlenk techniques. In a typical synthesis of CFTS nanocrystals with the wurtzite structure, 1 mmol $Cu(acac)_2$, 0.5 mmol $Fe(acac)_3$ and 0.5 mmol $SnCl_4.5H_2O$ were mixed with 10 mL of oleylamine (OLA) in a four-neck flask and stirred under vacuum for 30 min at room temperature and then back-filled with nitrogen. The solution was subsequently heated up to 150 °C and a mixture of 0.37 ml1-dodecanethiol (1-DDT) and 2.63 ml *tert*-dodecanethiol (*t*-DDT) quickly injected into the solution under nitrogen atmosphere with continuous stirring. The solution was subsequently heated up to 210 °C and maintained for 30 min. After reaction, the mixture was cooled down to room temperature and the products precipitated with a mixture of hexane and ethanol via centrifugation. A similar procedure was used for the synthesis of phase-pure zinc blende CFTS nanocrystals at 310 °C, using a mixture of 8 mL 1-octadecene (ODE) and 2 mL oleic acid (OA) as solvents.

Table S1. Composition (from EDX Analysis) of CFTS nanocrystals with wurtzite structure (using OLA as solvent) and zinc blende structure (using ODE and OA as solvents).

Sample	Structure	Cu: Fe: Sn: S	Cu/ (Fe+Sn)	Fe/ (Fe+Sn)	S/ (Cu+Fe+Sn)
a	Wurtzite	2.00: 0.93: 0.92: 3.72 (26.43: 12.35: 12.12: 49.10)	1.08	0.50	0.96
b	Zinc blende	2.00: 0.94: 0.86: 3.79 (26.34: 12.42: 11.38: 49.86)	1.11	0.52	0.99

Note: For sample (a) 25% excess of the $Fe(acac)_3$ precursor was used for the synthesis.

SEM images of CFTS nanocrystals synthesized in different solvents

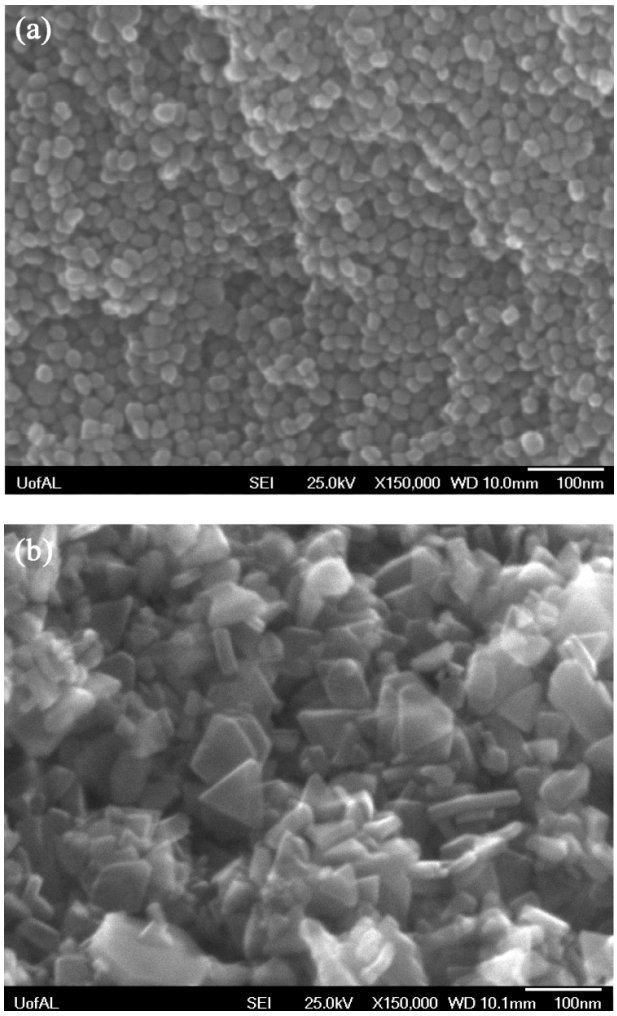

Figure S1. SEM images of (a) wurtzite CFTS nanocystals synthesized at 210 ^{o}C in OLA, and (b) zinc blende CFTS nanocystals synthesized at 310 ^{o}C in a mixture of ODE and OA.

Simulated crystal structure of wurtzite and zinc blende Cu_2FeSnS_4

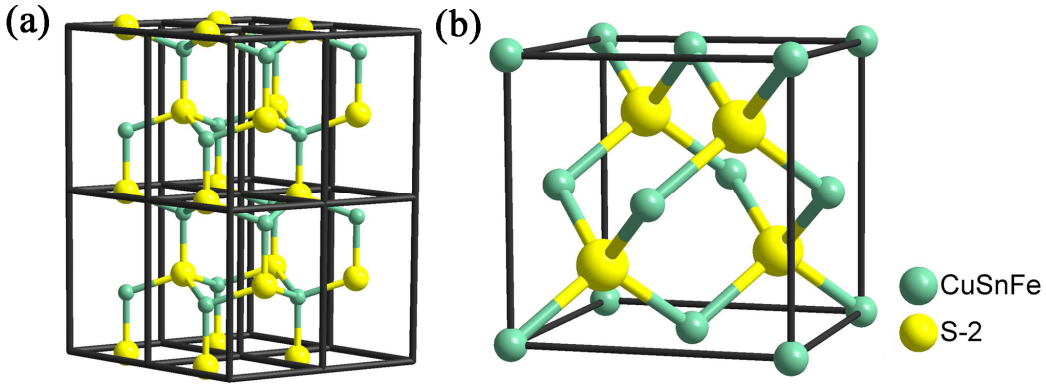

Figure S2. Crystal structures of (a) wurtzite (b) zinc blende Cu_2FeSnS_4.

Crystal data:

Formula	Cu_2FeSnS_4	
Crystal Structure	Wurtzite	Zinc blende
Space Group	$P6_3mc$ (No. 186)	F-43m (No. 216)
Lattice Parameters	$a = b = 3.856$ Å, $c = 6.364$ Å	$a = b = c = 5.436$ Å

Atomic Coordinates:

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**Wyck.**	**x/a**	**y/b**	**z/c**
	Wurtzite				Zinc blende			
S	2b	1/3	2/3	0	4c	1/4	1/4	1/4
Sn	2b	1/3	2/3	0.3752	4a	0	0	0
Fe	2b	1/3	2/3	0.3752	4a	0	0	0
Cu	2b	1/3	2/3	0.3752	4a	0	0	0

The structure of wurtzite and zin blende Cu_2FeSnS_4 can be obtained from that of ZnS by substitution of Zn(II) with Cu(I), Fe(II) and Sn(IV). The sulfur ion remains the same, coordinating with Cu(I), Fe(II) and Sn(IV) equally. In the crystal structure, Cu, Fe and Sn atoms statistically occupy the same position, with the occupation for each atom being 50%, 25% and 25%. Since the standard XRD pattern for wurtzite and zinc blende CFTS is not available in the database, we simulated the diffraction pattern based on the structure shown in Figure S2.

XRD patterns of binary and ternary sulfides

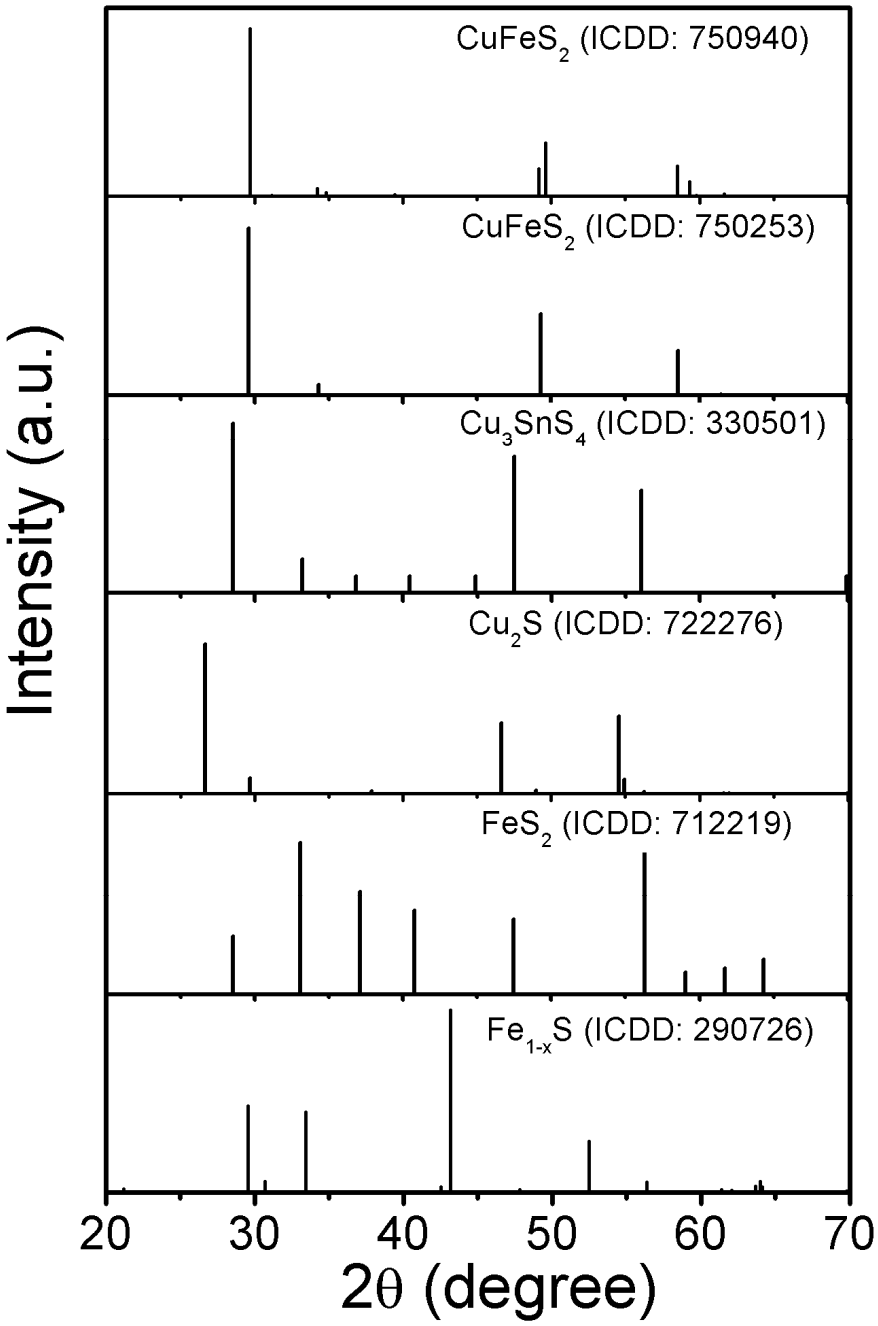

Figure S3. Standard XRD patterns of some binary and ternary sulfides.

XRD patterns of CFTS nanocrystals synthesized at different temperatures

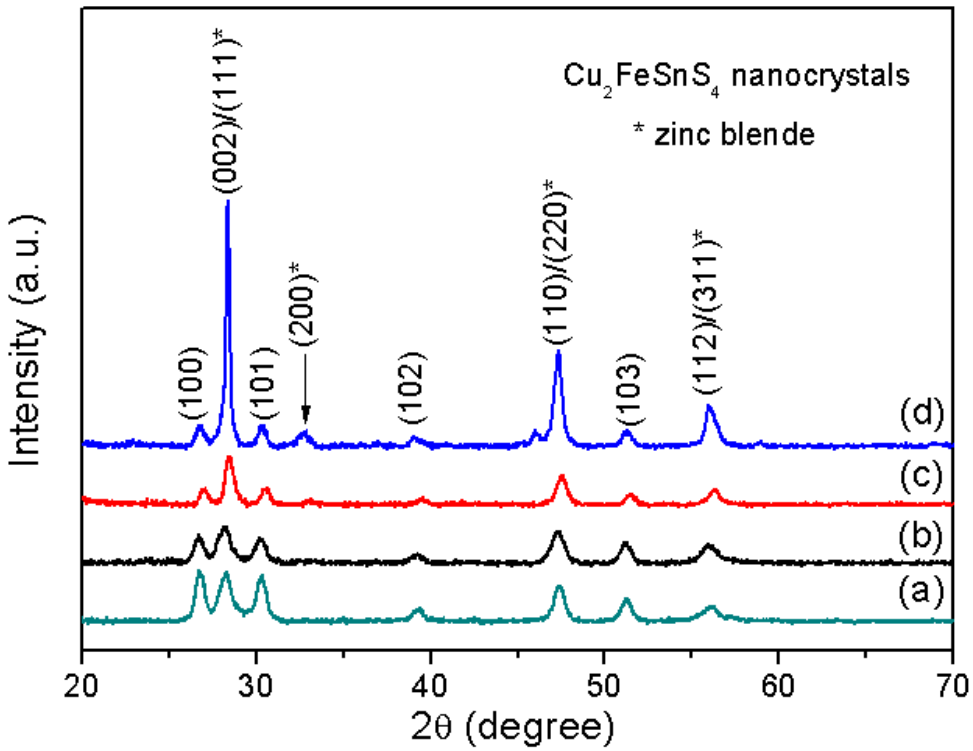

Figure S4. XRD patterns of the Cu_2FeSnS_4 nanocrystals synthesized at (a) 210, (b) 240, (c) 280, and (d) 310 ^oC using a mixture of 0.25 mL 1-DDT and 1.75 mL *t*-DDT as sulfur source. The peak around 32.8^o corresponds to the (200) planes of zinc blende CFTS nanocrystals.

XRD patterns of CFTS nanocrystals synthesized using different iron precursor

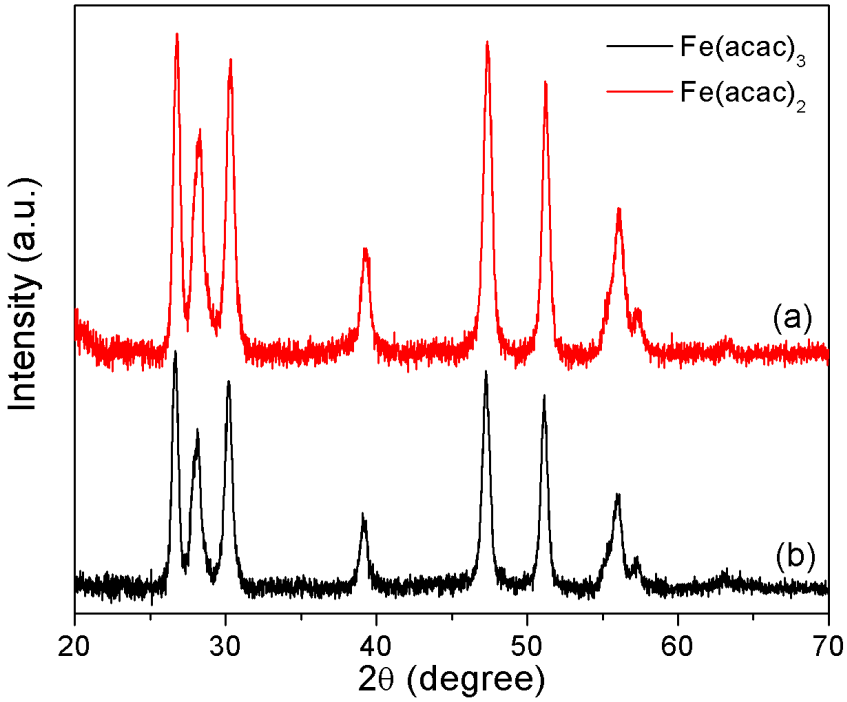

Figure S5. XRD patterns of the Cu_2FeSnS_4 nanocrystals synthesized using (a) $Fe(acac)_2$, (b) $Fe(acac)_3$ as precursor.